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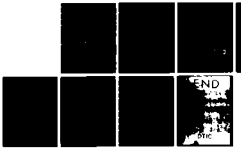

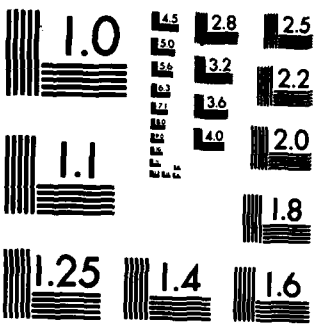
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ION MICROSCOPY OF METALS

AND SEMICONDUCTORS

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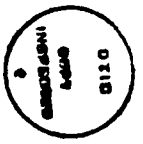

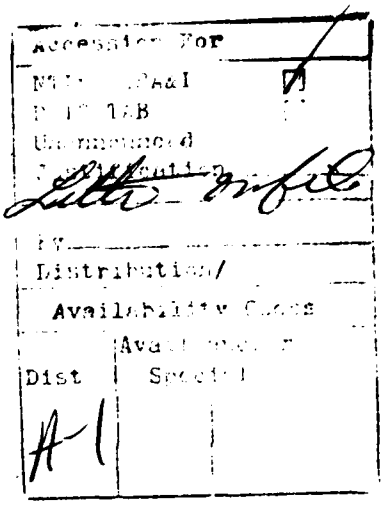

ION MICROSCOPY OF METALS AND SEMICONDUCTORS

INTRODUCTION

During the last year several major changes have been instituted to improve the performance of CAMECA IMS-300 ion microscope system at the Naval Research Laboratory. The computer system dedicated to the instrument has been replaced, and new maintenance procedures have reduced electronic and vacuum problems associated with the instrument. Because of this, the overall reliability of the system has been improved, and the total turn around time necessary for SIMS analyses has been reduced. The utilization of the ion microscope for collaborative scientific research at NRL has been greatly improved.

COMPUTER SYSTEM

The DEC PDP 11/20 computer that controlled the CAMECA IMS-300 ion microscope was replaced with an Apple IIc computer. Typically the PDP 11/20 computer had one to three down periods per year that required the assistance of a DEC service engineer to repair. Two to four weeks normally elapsed before the system was back on line. The Apple IIc computer is much more reliable, and a temporary replacement computer will be available while any hardware problems are being repaired. Thus, the total down time of the system from computer related problems can be expected to be reduced from about six to eight weeks per year to less than one week per year.

A new interface was built by D. Kidwell (Code 6170) between the Apple IIc computer and the CAMECA IMS-300 ion microscope. This interface controls the magnetic field strength of the instrument by a 16 bit digital-to-analog (DAC) converter, and detects and counts pulsed from the electron multiplier and photomultipliers of the CAMECA IMS-300 detection system. The detector interface includes a Schmitt trigger to discriminate between pulses produced when ions impinge upon the first stage of the electron multiplier and noise produced at other stages of the detector.

The software was rewritten from FORTRAN to BASIC and Assembly Language. The system can now acquire data during depth profiling, perform short range mass scans, list data that has been acquired on a line printer, store the data on floppy disks, convert secondary ion intensities vs. times to concen-

trations vs. depths, and print figures of the depth profiles. A long range mass scan routine to quickly scan the nominal masses from 1 to 250 will soon be completed, along with the associated software to print the results.

CAMECA IMS-300 ION MICROSCOPE

Scheduled maintenance periods have increased the overall reliability of the CAMECA IMS-300 ion microscope, and resulted in a substantial reduction in the total down time of the instrument. During this year the instrument was down for less than 10 days for unscheduled maintenance. The increased reliability of the overall system has resulted in the timely analyses of specimens by ion microscopy at the Naval Research Laboratory.

SECONDARY ION MASS SPECTROMETRY RESEARCH

During the last year, 214 different specimens were analyzed by secondary ion mass spectrometry (SIMS) at NRL. The principal investigators with whom collaborative projects were undertaken included 8 research scientists in the Chemistry Division (Code 6100), 9 research scientists in the Electronics Technology Division (6800), 2 research scientists in the Optical Sciences Division (6500), and 1 research scientist in the Tactical Electronic Warfare Division (Code 5800). Several other collaborations occurred with research scientists from outside of NRL, including the Bureau of Printing and Engraving, the Night Vision and Electro-Optics Laboratory at Ft. Belvoir, the Chemistry Department at Cornell University, the Electrical Engineering

Department at Purdue University, and the Electrical Engineering Department at Brown University. The results and conclusions of these investigations have been presented in 57 memorandums and 5 letters. These efforts have resulted in one publication and one presentation at a scientific meeting during this year, and are expected to result in several more during the coming year. The results of many of these collaborations are summarized below.

1. Chemistry Division

Collaborators within the Chemistry Division included R. Jeffries (Code 6110), A. Berry (Code 6137), S. Gadomski (Code 6130), H. Ladouceur (Code 6174), I. Singer (Code 6176), R. Colton (Code 6177), D. Kidwell (Code 6177) and N. Turner (Code 6177).

The thickness, uniformity, and elemental composition of a Nb thin film deposited on a Si substrate were determined by SIMS for A. Berry (Code 6137). The Nb film was fabricated from an organometallic material. Also, mass scans were performed to determine trace elemental impurities in the film.

The elemental composition of an orange particle embedded in an aircraft window was determined for S. Gadomski (Code 6130). It was concluded from the elemental composition of the particle as determined by SIMS and the density of the particle that the particle was a mineral.

The rate of Au growth by a vapor deposition instrument was determined for H. Ladouceur (Code 6174). Specimens of thin Au layers deposited on Si substrates for 2, 4, 8 and 16 minutes, respectively, were depth profiled by SIMS. From the respective

depths of these layers, the rate of deposition was determined. Also, the lateral homogeneity of the thicknesses of the Au layers was evaluated.

The incorporation of Ti in the near surface region of steel by ion implantation has previously been determined to increase the wear properties of steel. During the Ti implantation, C from the residual atmosphere of the implanter was also incorporated. This simultaneous incorporation of C has been enhanced by backfilling the implanter with carbon monoxide. The use of enriched ^{13}CO allowed the differentiation of the incorporated C from the residual C already in the steel. SIMS, an isotopically sensitive technique, was used to determine the depth profiles of the two isotopes of carbon. The profiles of the implanted Ti and the matrix element Fe were also simultaneously determined. Auger Electron Spectroscopy was used to analyze these specimens, and the results of the two techniques have complimented each other.

In collaboration with I. Singer (Code 6176), SIMS analyses have determined the distributions of Ti, Fe, ^{12}C from a series of 52100 steel specimens. Different specimens of this steel were implanted at different temperatures. At increased temperatures, the ^{13}C diffused towards the surface, and at the highest temperatures only terrestial ratios of C were determined. The incorporated ^{13}C had diffused out of this specimen.

Another study characterized the diffusion of the carbon in different types of Ti implanted steels that were heated during implantation. From the isotopic ratios of carbon determined by

SIMS, it was determined that in steels with low amounts of residual carbon, the ^{13}C was incorporated into the steel. In high carbon steels, the carbon from the steel diffused towards the surface. The enriched ^{13}C from the ^{13}CO in the Ti implanted region was reduced by nearly two orders of magnitude in concentration.

2. Electronics Division

Collaborators within the Electronics Division included B. Molnar (Code 6812), H. Dietrich (Code 6812), W. Schmidt (Code 6813), R. Henry (Code 6821), N. Bottka (Code 6821), J. Comas (Code 6823), W. Beard (Code 6823), P. Klein (Code 6822) and R. Kaplan (Code 6834).

In collaboration with B. Molnar (Code 6812) the redistribution of Be in heat pulsed and furnace anneals of implanted InP has been determined by SIMS. The SIMS part of the study, which was begun by G. Ramseyer while he was a graduate student at Cornell University, was finished during this year at the Naval Research Laboratory. The results were presented at the Materials Research Society Meeting in Boston in November 1983, and published in the proceedings, Vol. 27 in 1984.

The redistribution of similarly implanted Be in InAs and GaInAs was also characterized by SIMS. The distributions of Be and Cl in InP from implanted $BeCl^+$ have been determined by depth profiling, and compared with those distributions for Be^+ implantation.

The research of Be implanted InP has now advanced so that contacts are being fabricated on the semiconductors. Several studies have been completed which compared the redistributions of the Au, In, P and Be vs. annealing conditions. Also, the distributions of Be implanted through the Au contacts into the InP matrix were investigated.

The quantification of As in InP was determined by SIMS for InP crystals grown by R. Henry (Code 6821). The As was incorporated into the crystals while they were being grown. SIMS standards were fabricated by B. Molnar (Code 6812)(by ion implantation. Of original interest was the homogeneity of the As in different locations of the crystal. However, the inhomogeneity of the InP matrix reduced the accuracy of the quantification of As in these InP crystals. The effect of changes in the ratio of III to V elemental compositions in these types of semiconductor materials is being investigated by SIMS, X-ray Photoelectron Spectroscopy, and Auger Electron Spectroscopy.

The depth profiling capabilities of SIMS makes it an ideal method to determine the distributions of matrix elements in epitaxial layers. Because of the high sensitivity that SIMS has for most elements, the distributions of many n- and p- dopants grown in epitaxial materials can only be directly determined by SIMS depth profiling.

The profiles of the matrix element Al in molecular beam epitaxial (MBE) grown multilayered GaAs/AlGaAs semiconductor specimens were determined for J. Comas (Code 6823). Similar

specimens grown by molecular chemical vapor deposition (MCVD) by N. Bottka (Code 6821) were also analyzed. From these results, these two methods of crystal growing have been compared.

The high temperature annealing of MBE grown AlGaAs layers on a GaAs substrate without a cap can result in the evaporation of the AlGaAs layer. The reduction in the thicknesses of the AlGaAs layers vs. annealing conditions was determined by SIMS depth profiling in collaboration with J. Comas. Also, a MBE grown specimen was depth profiled which had been fabricated by ramping the Al in AlGaAs layers grown between GaAs layers. These depth profiles were used to evaluate the precision in fabricating III-V materials by MBE.

Because of its high sensitivity for most elements, SIMS can determine not only matrix elements, but also elements present in trace concentrations. In collaboration with J. Comas, several GaAs layered specimens with buried Be n-doped layers grown by MBE were analyzed by depth profiling. Of interest were the depth profiles of the redistributed Be for the specimens which had been annealed under different conditions. From these results the diffusion coefficients for Be in GaAs will be calculated.

Multilayered Be doped MBE grown GaAs matrix specimens were depth profiled for J. Comas. Also, similarly grown MCVD specimens were analyzed for N. Bottka. The quantification of these layers was accomplished with ion implanted standards.

Si doped MBE and MCVD grown GaAs specimens were also analyzed for J. Comas and N. Bottka, respectively. However, the detection limit of the CAMECA IMS-300 ion microscope for Si is

only about $4x10^{17}$ atoms/cm^3. Increased SIMS sensitivity for Si in this matrix is possible using a cesium ion source. J. Comas had the Si doped MBE specimens reanalyzed at Bell Laboratory with a CAMECA IMS-3f ion microscope. N. Bottka's MCVD specimens are scheduled to be analyzed by Dr. Morrison of the Chemistry Department at Cornell University with a cesium source on their CAMECA IMS-3f ion microscope. Virtually all of the state of the art ion microscopes now have cesium ion sources, and it is recommended that the Naval Research Laboratory consider upgrading the CAMECA IMS-300 ion microscope with such a source.

SIMS depth profiles of As in Si were determined for H. Dietrich (Code 6812). It was at first necessary to determine the analytical method which gave the highest sensitivity for this determination using the CAMECA IMS-300 ion microscope. Comparisons were then made of the As distributions for furnace annealed, proton annealed, and self annealed specimens vs. the as-implanted specimen. Also, it was determined that oxygen was incorporated into the furnace annealed specimen during its annealing.

SIMS was also used to determine the profiles of N implanted SiO_2 capped, Si substrates for H. Dietrich (Code 6812). Because of molecular interferences, several different approaches were investigated to determine the best procedures for the analyses. A series of specimens, each heated at different temperatures during the implantation so that each was simultaneously annealed, was depth profiled. To complete the

quantification of these materials, a series of implanted standards are being fabricated by ion implantation.

The relative concentrations of impurities is SiO_2 films on Si substrates were determined by SIMS for W. Schmidt (Code 6813). Ion microscopy was used to determine the locations of the impurities, and the elemental compositions of particles adhering to the surfaces. It was determined that the principal source of contamination was a NaOH solution used to remove the photoresist during the fabrication process.

Methodology was developed to depth profile epitaxial layers of Fe/SiC grown on Si substrates for R. Kaplan (Code 6834). The differences in the elemental distributions for the as-grown and annealed specimens were determined.

SIMS was used to identify the elemental composition of a film on a specimen submitted by N. Bottka (Code 6821). The specimen was from the inside of the MCVD instrument at the Naval Research Laboratory. From the elemental composition of the film, it was determined that the film was stainless steel. Several other potential sources of the film were eliminated from consideration.

3. Optical Sciences Division

Collaborators within the Optical Sciences Division included E. West (Code 6571) and C. Bulmer (Code 6571). These researchers have been interested in determining the distributions of Ti diffused $LiNbO_3$. Similar matrices of Mg:$LiNbO_3$ and Sr:$BaNbO_3$ have been analyzed. These materials were fabricated by depositing thin layers of TiO_2, and then heating the

materials so that the Ti diffused into the substrates. From the profiles of the Ti, diffusion coefficients have been determined for Ti in these matrices.

Because Fe reduces the transmission properties of these $LiNbO_3$ materials, the quantification of trace amounts of residual Fe was made by SIMS. Standards were fabricated by ion implantation, and residual Fe concentrations of 2.5 ppm were determined.

4. Others

NRL Prob. #61-M053-X-3 was addressed by SIMS. Depth profile analyses of two specimens that had dielectric layers sandwiched between thin layers of aluminum and polyethylene terephthalate substrates were performed for J. Desmond of the Bureau of Engraving and Printing. SIMS mass scans determined the major elements associated with each of the layers. SIMS depth profile analyses determined the distributions of the major elements,and the amount of diffusion between the layers. Also, the thicknesses of each of the layers were determined. A unique layer was identified in one of the specimens.

Several projects have been undertaken in collaboration with J. Dinan of the Night Vision and Electro-Optics Laboratory at Ft. Belvoir, VA. His interests are in II-VI semiconductor materials. Depth profiles of In in MBE grown CdTe/CdTe materials profiled at NRL with the CAMECA IMS-300 ion microscope were compared to profiles previously obtained by Evans and Associates using a CAMECA IMS-3f ion microscope. The results were similar.

Depth profiles of the matrix elements by SIMS were performed on MBE grown HgCdTe/CdTe specimens for J. Dinan. Also, trace element contaminants were first determined by mass scans, and then depth profiled. A specimen fabricated by a new growth process, know as Ionized Cluster Beam Epitaxy (ICBE), was also depth profiled by SIMS for J. Dinan. The specimen submitted was CdTe/Si. The profiles of the matrix elements, and trace contaminants, were obtained.

FUTURE PRESENTATIONS OF THIS RESEARCH

SIMS is one of several surface analyses techniques available in the Chemistry Division at the Naval Research Laboratory. During the last several months, Dr. Ramseyer (Code 6177) has been learning the mechanics of X-ray Photoelectron and Auger Electron Spectroscopies. In particular, in collaboration with R. Colton (Code 6177) and N. Turner (Code 6177), InP, GaAs, and AlGaAs materials which have exhibited matrix effects by SIMS are being analyzed by these methods. The further characterization of these materials should lead to a better understanding of the matrix effect in SIMS. This should result in improved SIMS quantifications of III-V semiconductor materials. Based upon the preliminary results of this work, an abstract has been submitted for presentation at the AVS meeting in December 1984.

The results of the Ti implanted steel samples in collaboration with I. Singer, in conjunction with Auger Electron Spectroscopy (AES) determinations by R. Jeffries (Code 6110), will be submitted for presentation at the SIMS V in 1985. The

emphasis will be on the quantification of the Fe-Ti materials by SIMS, and on the complimentary information obtained from these materials by SIMS and AES.

Other SIMS research which is of interest to the scientific community, and which will be presented, include the analytical methodology developed for the SIMS analyses of $LiNbO_3$, and the quantification of trace concentrations of Fe in this matrix. The analytical procedures developed for the SIMS analyses of these materials will be submitted to the 1985 Pittsburgh Conference. The redistribution of Be in InP with Au contacts should be completed in the next few months, and a comparison study of MCVD and MBE layers of Be and Si doped GaAs materials is nearly completed. These studies will be presented in appropriate conferences determined in collaboration with B. Molnar, J. Comas and N. Bottka, respectively.


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